ARE MOLECULES AT SURFACES SOLVATED BY SUPERCRITICAL FLUIDS DIFFERENTLY THAN IN SOLUTION?

Frank V. Bright*, Philip M. Page, Chase A. Munson, Wendy E. Gardinier, Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, New York, 14260-3000 USA

chefvb@acsu.buffalo.edu 716-645-6963 (FAX)

We summarize our most recent work on how solutes are solvated at interfaces. Toward this end, we have prepared a series of model silica-based interfaces that have been "labeled" with a solvatochromic fluorescent probe molecule. The solvatochromic fluorophore serves simultaneously as the solute and an environment sensitive probe. Unlike in solution, adsorbed molecules can be surrounding by other adsorbates, they can be distributed within an ensemble of sites with differing physicochemical properties, or they can be located in sites that are inaccessible to solvent molecules. All of these scenarios are observed for dansylated controlled pore glasses in organic liquids and supercritical CO_2.

INTRODUCTION

Supercritical fluid chromatography (SFC), supercritical fluid extractions (SFE), and supercritical fluid-based cleaning (SFBC) are extremely powerful tools.[1-4] In each technique an interface of sorts plays a key role in the separation outcome (SFC), the extraction efficiency (SFE), or the degree of cleaning (SFBC). Unfortunately, nearly all work on solute-fluid, solute-solute, and solute-cosolvent interactions in supercritical fluids and mixtures has focused on studying ***solutions***. Thus, although it is clear that information on the intermolecular interactions between supercritical fluids, cosolvents, and ***interfaces*** is key to advancing our understanding of supercritical fluid-based cleaning, extractions, or separations, little work has appeared on this subject.

Herein we describe a portion of our work on the investigation of a model solute covalently attached to an interface in the presence of organic liquids and supercritical CO_2 ($scCO_2$).

MATERIALS AND METHODS

Figure 1 illustrates our model systems. The probe for our experiments is dansyl. Dansyl was chosen because it is reasonable fluorescent and its fluorescence emission spectra shift in a predictable manner that depends on the physicochemical properties of the solvent (Figure 2). Dansyl has also been used previously to probe silica interfaces.[5]

Two systems were evaluated: (a) dansyl propylamide (DPA) and (b) dansyl attached to

the surface of aminopropyl controlled pore glass (D-CPG). The DPA experiments were used as controls to monitor how the probe itself was solvated. The D-CPG experiments were carried out to probe an interface. The D-CPG experiments were also conducted on a series of samples that had different surface concentrations of dansyl to amine (saturation to 10^{-5}:1). Experiments were conducted initial using liquids (hexane, chloroform, ethyl acetate, 1-octanol, 1-butanol, 1-propanol, and methanol). Experiments were then extended to pure $scCO_2$ (35 °C) between a reduced density of 0 (vacuum) and 2.0.

The D-CPG samples were prepared in a five step process. Step1: 0.5 g of amino-propylated controlled pore glass was added to 30 mL of dry MeCN under N_2 (g) in a dry round bottom flask. Step 2: Dansyl chloride was dissolved in dry MeCN and introduced into the flask via a syringe. The molar ratio of dansyl:amine was 10:1 (saturated), 1:1, 0.1:1, 10^{-2}:1, 10^{-3}:1, 10^{-4}:1, and 10^{-5}:1. Step 3: Two equivalents of triethylamine was added to the reaction mixture and the reaction flask was heated to 50 °C for 24 h under Ar (g). Step 4: The dansylated particles were washed with EtOH, Water, MeCN, and hexane. Step 5: The particles were dried in a vacuum oven for several hrs at 70 °C.

The particles for study are loaded into a glass melting point capillary. For the liquid experiments, the capillary and its contents were soaked in a given solvent and the measurements carried out while the particles are solvated. For the $scCO_2$ experiments, the particles/melting point capillary were positioned within our standard high pressure cell. The high-pressure cell was initially evacuated to remove any non-specifically adsorbed species on the D-CPG surface and experiments were performed from low to high density. Control experiments demonstrate that there is no hysteresis.

The excitation wavelength for all experiments is 350 nm. All fluorescence measurements were performed by using an SLM 48000 MHF.

The blank contribution was < 2%.

RESULTS AND DISCUSSION

The Lippert expression provides a link between the physicochemical properties of the solvent and the observed spectral shift:

$$\nu_A - \nu_F = 2/hc\ [((\varepsilon-1)/(2\varepsilon+1)) - ((n^2-1)/(2n^2+1))][(\mu_E-\mu_G)^2/a^3] + \text{constant} \qquad (1)$$

where ν_A and ν_F are the absorbance and emission maximum (cm^{-1}), respectively, h is Plank's constant, c is the speed of light, a is the radius of the cavity swept out by the fluorophore, μ_E and μ_G are the fluorophore's excited- and ground state dipole moments, respectively, and ε and n are the solvent dielectric constant and refractive index, respectively. The term that is a function of ε and n is called the orientational polarizability, ΔF.

Figure 3presents the Lippert plots for DPA and D-CPG (dansyl:amine = 10:1 (saturated), 1:1, 0.1:1, 10^{-2}:1, 10^{-3}:1, 10^{-4}:1, and 10^{-5}:1). The results of these experiments

show several interesting trends. First, the molar ratio of dansyl:amine has a substantial affect on the cybotactic region that surrounds the dansyl probe. This result means that the surface that were are probing is dictated by the probe concentration. In a general sense, the cybotactic region is very polar at high dansyl:amine ratios and the dipolarity drops significantly as the probe concentration is decreased. This result is better visualized in Figure 4 where we present the Δ Stokes Shift (D-CPG Stokes Shift - DPA Stokes Shift in a given solvent) vs. ΔF. The point at which these graphs cross zero provide a rudimentary measure of the dipolarity surrounding the D-CPG interface. For example, at 10:1 dansyl:amine the environment is extremely dipolar ($\Delta F \sim 0.27$), but at 10^{-5}:1 dansyl:amine the environment is much less dipolar ($\Delta F \sim 0.15$).

Our interpretation of these data are as follows. For the 10:1 and 1:1 particles, the dansyl is in the most dipolar environment and the dansyl molecules are surrounded by other dansyl molecules (μ_G dansyl = 3.0 D). As we lower the dansyl:amine (0.1:1, 10^{-3}:1, and 10^{-4}:1) the dipolarity that the dansyl senses decreases and the dansyl is more sensitive to solvent. This is consistent with the know dipole moments of free amines (μ = 1.4 D) and hydroxyl groups (μ = 1.5 D). As we proceed to the lowest dansyl:amine materials, the environment is the least dipolar. This is consistent with the dansyl residues reporting from an environment rich in silicon dioxide (μ = 0.6 D) that is not particularly accessible to solvent.

In Figure 5 we present the Stokes Shift results for DPA and D-CPG (10:1, 1:1, and 0.1:1) as a function of the refractive index cross term in $scCO_2$. We can see that all the spectra shift red with an increase in the $scCO_2$ density. This result arises from the increasing CO_2 solvent strength with density and the increased solvation of the dansyl residues by the added $scCO_2$. We can also see (Figure 6) that the absolute dansyl shift (|Stokes Shift in Vacuum - Stokes Shift in $scCO_2$|) is a strong function of the dansyl:amine ratio. Specifically, when the dansyl:amine is high the absolute shift is small. This result is consistent with the surface being highly dipolar and the addition of CO_2 only slightly being able to augment the dipolarity of the surrounding dansyls. As the dansyl:amine ratio decreases, the mean free distance between dansyl residues decreases and the CO_2 now has more access to the surface/dansyl residues and the surface is more sensitive to an increase in solvent strength.

Figure 7 summarizes the effects of dansyl:amine ratio, solvent, and $scCO_2$ on a model interface.

CONCLUSION

Solvation at an interface is much different than solvation of "isolated" molecules in solution. Unlike in solution, adsorbed molecules can be surrounding by other adsorbates, they can be distributed within an ensemble of sites with differing physicochemical properties, and/or they can be located in sites that are inaccessible to solvent molecules. All of these scenarios are observed for dansylated controlled pore glasses in organic liquids and supercritical CO_2. Specifically, at the highest loading of dansyl at the surface, the dansyl molecules are solvated by other dansyls and solvent does not access the dansyls to modulate their cybotatic region to any significant level. As the dansyl loading decreases, the mean free

distance between these molecules decreases, the cybotactic region surrounding the dansyl residues encounter changes, and solvent is able to access/solvate the dansyl. However, the extent of solvation is never like that seen for isolated dansyl molecules in solution. As the adsorbate concentration is decreased further, one would anticipate the isolated molecule case to occur. This is not so because dansyl molecules distribute themselves to an inaccessible, SiO_2-rich site on the CPG surface.

REFERENCES

[1] *Supercritical Fluid Chromatography*; Smith, R.M., Ed.; Royal Society of Chemistry Monograph: London, UK, 1988.

[2] McHugh, M.A.; Krukonis, V.J. *Supercritical Fluid Extraction - Principles and Practice*; Butterworths: Boston, MA, 1993.

[3] McHardy, J.; Sawan, S.P. *Supercritical Fluid Cleaning: Fundamentals, Technology and Applications*, 1998.

[4] Tseng, H.-S.; Purtell, R.; Rothman, L. *Process. Adv. Mater.* **1994**, *4*, 197.

[5] Lochmuller, C.H.; Marshall, D.B.; Wilder, D.R. *Anal. Chim. Acta* **1981**, *130*, 31.

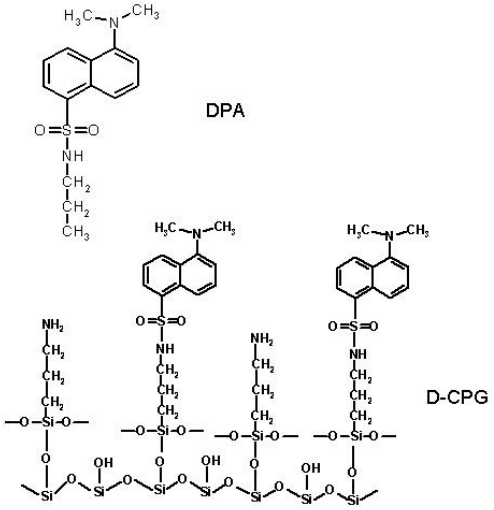

Figure 1. The systems.

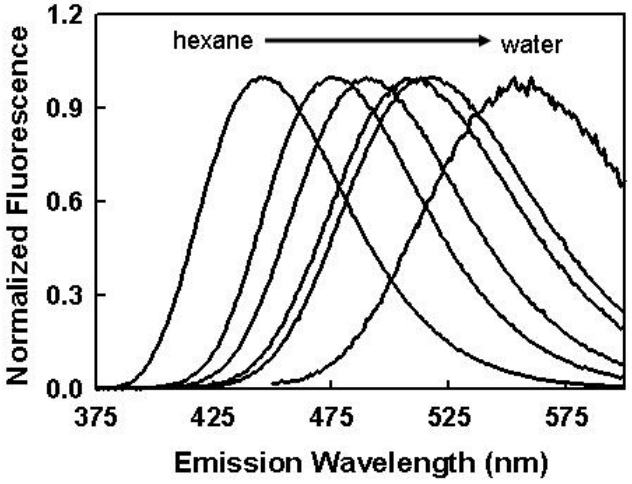

Figure 2. Solvent dependent DPA spectra.

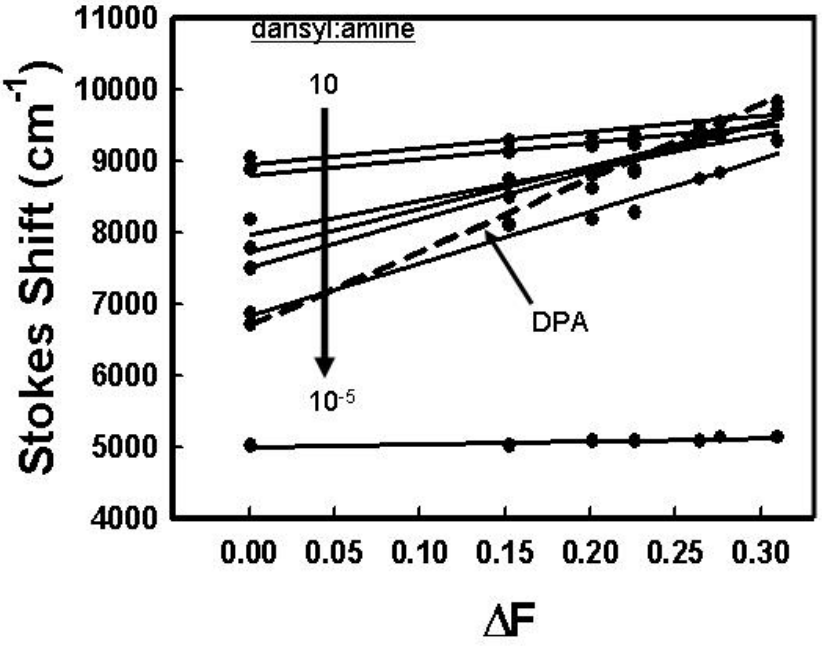

Figure 3. Lippert plots for DPA and D-CPG in organic liquids.

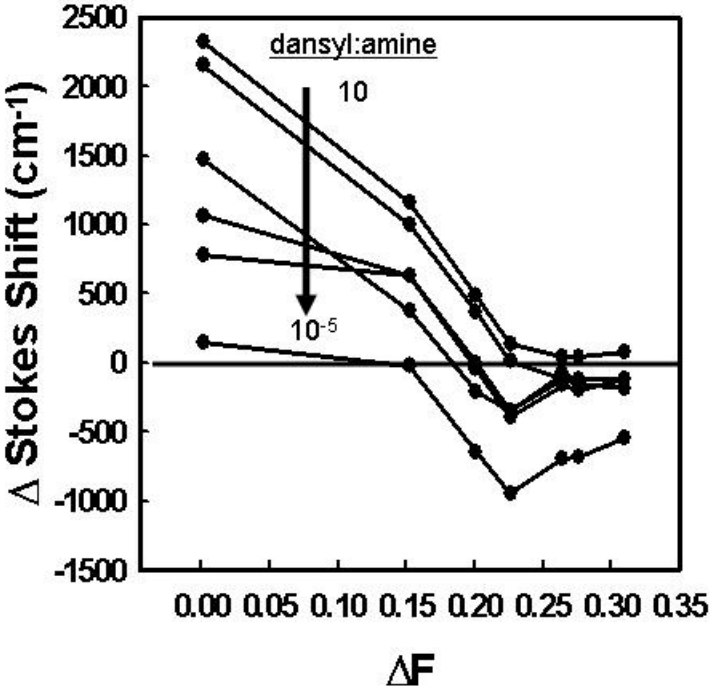

Figure 4. Differential Lippert plot for D-CPG.

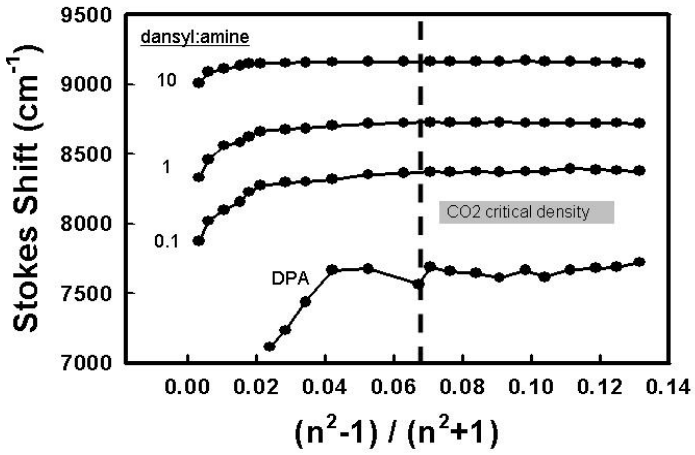

Figure 5. Stokes shift vs. refractive index cross term in $scCO_2$.

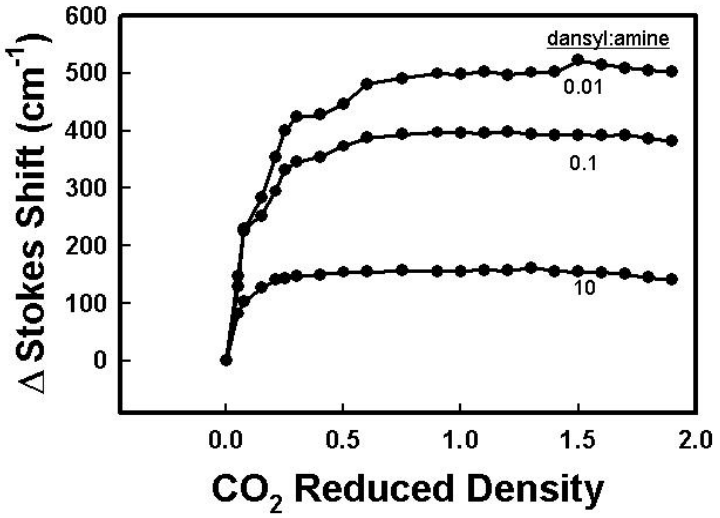

Figure 6. Differential Stokes shift vs. CO_2 Density for D-CPG.

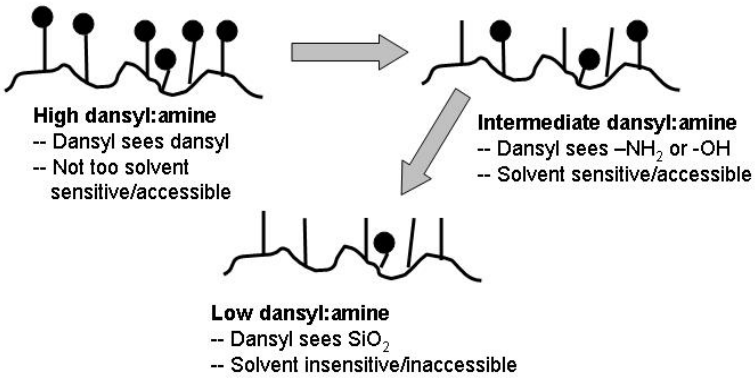

Figure 7. Summary model